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Investigation of Copper-Chalcopyrite Thin Films from Nanoparticle Powder

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Abstract

Chalcopyrite $CuIn_{0,5}Ga_{0,5}Se_2$ (CIGS) thin films for photovoltaic applications from nanoparticle powder were investigated in this work. CIGS nanoparticle powder was synthesized by mechanical allowing process from the mixture of elemental Cu, In, Ga and Se precursors in a cylindrical steel vial under argon atmosphere. CIGS fine-grains with diameter in the range of 100-140 nm were obtained. The CIGS powder was then deposited onto glass and silicon substrates by the thermal evaporation technique. The X-ray diffraction, transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy analysis (EDS) measurements were used to describe the structure and morphology of CIGS layers. From X-ray diffraction spectrum, the evaporated CIGS are polycrystalline in nature and exhibiting chalcopyrite phase. From the across-section TEM micrographs of CIGS films, we evaluated the thickness of the CIGS layers about 1 µm and the lattice spaces have been determinate from the high resolution transmission electron microscopy (HRTEM) micrographs.

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Keywords: $CuIn_{0,5}Ga_{0,5}Se_2$ nanoparticle ; structural properties.

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1. Introduction

Copper-chalcopyrites are a class of copper compounds and alloys that assume a tetrahedral crystal structure with various chemical compositions [1]. Thin film solar cells based on copper-chalcopyrite have been widely investigated because of their potential optoelectronic properties for photovoltaic applications [1-5]. Among these, copper indium gallium diselenide ($CuIn_{1-x}Ga_xSe_2$)-based solar cells have achieved a record efficiency of 19.9% at the laboratory scale [6]. Recently, scientific and technologic research efforts have focused on development of solar cells based on $CuInGaSe_2$ nanoparticles [7-11].

In our previous paper [12] we have reported on investigation of $CuIn_{0.5}Ga_{0.5}Se_2$ (CIGS) nanocrystalline powders prepared by mechanical alloying method. In this manuscript we study the structural properties of $CuIn_{0.5}Ga_{0.5}Se_2$ thin films, deposited on glass and silicon substrates, obtained from nanoparticle powder.

2. Experimental

The $CuIn_{0.5}Ga_{0.5}Se_2$ (CIGS) layers were grown on glass and silicon substrates by conventional thermal evaporation method. The $CuIn_{0.5}Ga_{0.5}Se_2$ nanocrystalline powder which was used as precursor of $CuIn_{0.5}Ga_{0.5}Se_2$ layers was synthesized by mechanical allowing technique. More details about CIGS nonoparticle powder process preparation are described elsewhere [12]. The growth procedure of evaporation was done in Balzers coating unit from a tungsten crucible under a vacuum of order 10^{-6} Torr. Prior to deposition the substrates were cleaned by a soap and ultrasonic bath. The glass and silicon substrates were kept at 300°C during the evaporation process.

The microstructure characterization of CIGS thin films was performed by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). XRD patterns were collected using a PHILIPS X'PERT instrument with Cu Kα (λ = 1.54056Å) radiation. The diffraction intensities were measured in the range from 2θ = 10° to 80° with a step width of 0.02°. TEM and high resolution transmission electron microscopy (HRTEM) measurements were performed using a JEO-2010CX operated at 200 kV. The specimen for TEM measurement was prepared by mechanical polishing, dimpling and Ar-ion milling. The TEM studies were made on CIGS films grown onto silicon substrates. Scanning electron microscopy (SEM) was applied in order to study the surface morphology of samples using a JSM JEOL 6400-scanning electron microscopy (SEM) coupled with an energy dispersive spectrometry (EDS) system.

3. Results and Discussion

The crystallographic structure of $CuIn_{0.5}Ga_{0.5}Se_2$ source powder was discussed in previous publication [12] which the chalcopyrite phase with the predominant growth direction [112] has been revealed and the calculated cell parameters are: a = 5,705 Å and c = 11,250 Å. This powder with average grain size of about 140 nm was then deposited onto glass and silicon substrates. The XRD spectrum of the CIGS thin films deposited on glass at 300°C substrate temperature is shown in figure 1a. From this diffractogram, we observed four reflections at 2θ = 26.68°, 44.85°, 52.58°, and 71.08° corresponding to (112), (220/204), (312/116) and (316) planes of the chalcopyrite phase by comparison with standard JCPDS data card of $CuIn_{0.5}Ga_{0.5}Se_2$ compound [13]. No other phases were detected. It has been also shown that the CIGS films exhibit strong preferential orientation along the (112) plane. The lattice parameters calculated from the X-ray diffraction data (a = 5,769 Å and c = 11,608 Å) coincide with the reported values (a = 5,694 Å and c = 11,312 Å) of T. Yamaguchi et al. [14]. The crystallite size determined from the Scherrer formula using the θ-value of the (112) diffraction peak is found as 10.3 nm.

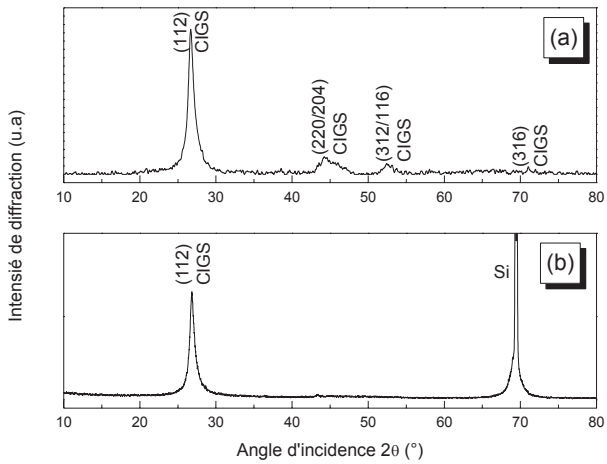

Figure 1: X-ray diffractogram of CIGS film deposited on (a) glass, (b) Si.

The XRD diffractogram recorded from CIGS layer grown on silicon substrate is displays in figure 1b. A strongest diffraction peak at around $2\theta = 69.35°$ of the silicon substrate were indexed. However, only one weak peak at $2\theta = 26.7°$ corresponding to (112) plane of CIGS phase was detected. The microstructural parameters of CIGS films deposited on glass and silicon substrates are presented in table 1. Those values are calculated from XRD peak position of the (112) planes.

The surface morphology of CIGS film deposited on glass substrate is depicted in figure 2. A high density of mostly rounded grains with sizes varied between 115 and 241nm was observed. The large difference in crystallite size values calculated from XRD data (10.3 nm) and SEM image may be due to that each grain observed under the SEM profile contains several individual nanocrystallites. The elementary composition obtained from EDS analysis is stoichiometric or slightly Cu-rich (Cu:In:Ga:Se = 26,4:13,6:11,0:49,0). A homogenous distribution of the constituent elements at the surface film is detected. The SEM plane-view of CIGS film deposited on silicon is presented in figure 3. It observed that the surface film is rough with granulose microstructure with grains sizes varied between 100 and 500 nm. Comparing with CIGS layer deposited on glass substrate, the CIGS film deposited on silicon shows irregular shape grains disposed on the surface film.

As a result, the CIGS films deposited on glass substrates have better crystalline characterizations and morphology than those deposited on silicon substrates. From the literature the enhancement in morphology and the strong (112)-orientation have been attributed to the presence of sodium (Na) by diffusion during growth from a soda-lime glass (SLG) substrate [15-18]. But for our samples we cannot compared the degree of orientation because the intensity of silicon substrate peak is dominated in CIGS films deposited as observed in XRD pattern and no interaction of the Na with Se is formed [19]. For these reasons, the strong orientation of substrate peak may be due to the thickness of CIGS film smaller than the penetrability of X-ray.

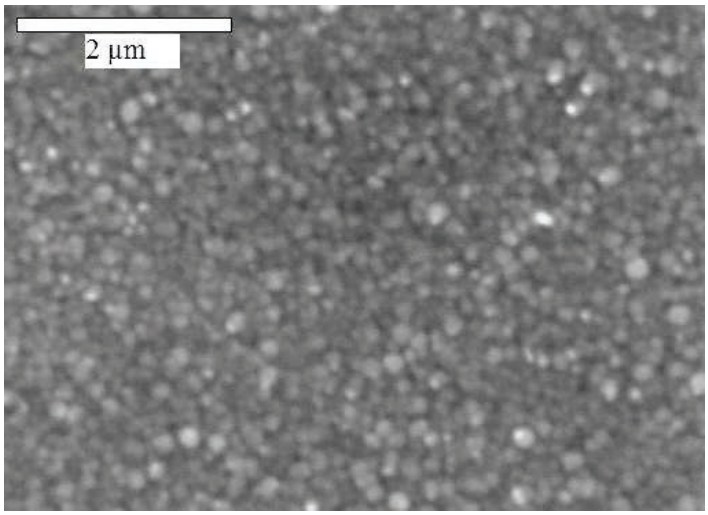

Figure 2: SEM image of CIGS film deposited on glass substrate.

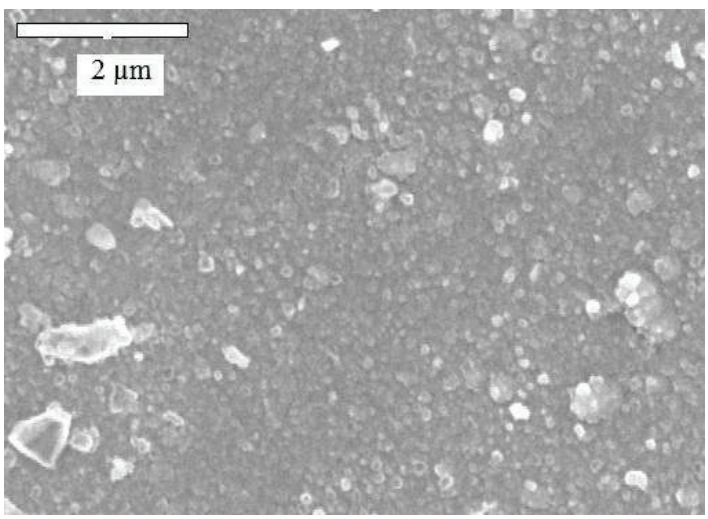

Figure 3: SEM image of CIGS film deposited on silicon substrate.

From the TEM cross-sectional view of the CIGS film deposited on silicon substrate, not shown here, the thickness of CIGS layer is found to be 1 µm. The high resolution transmission electron microscopy (HRTEM) observation of the CIGS film was displayed in figure 4. The HRTEM image shows a nanocrystalline characteristic with well defined plane orientations. Certain zones are marked to indicate the different atomic arrangement directions. These observations also confirm that the grain observed under the SEM profile may contain good number of individual nanocrystallites. The transmission electronic diffraction pattern obtained from the sample is presented as inset in figure 4. From this figure we observed two well defined rings which are characteristic of polycrystalline compounds. The

interplanar spaces estimated from these rings are $d_1 = 3.09 \pm 0.69$ Å and $d_2 = 1.89 \pm 0.34$ Å corresponding to the (112) and (220) planes of the CIGS chalcopyrite phase. Those values are comparable to the reported ones (3.6 Å) [20].

Table 1: Structural parameters of CIGS films calculated from XRD peak position of (112) planes.

Substrate	Interplanar distance (Å)	FWHM (°)	Crystallite size (nm)	Strain x 10^{-3}	Dislocation x 10^{-3}lin/nm^2
glass	3.339	0.783	10.3	6.62	9.426
silicon	3.336	0.712	12	3.34	6.944

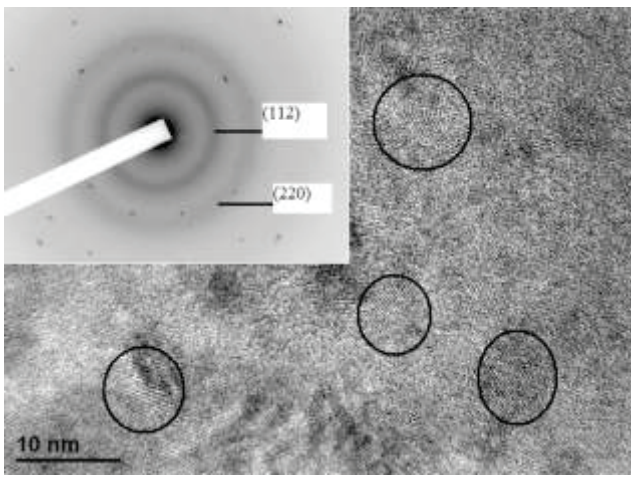

Figure 3: Microstructure of CIGS film observed by HRTEM. Inset shows the transmission electronic diffraction pattern of CIGS film.

1. Conclusions

In this work, using the alloyed $CuIn_{0.5}Ga_{0.5}Se_2$ nanoparticle powder, $CuIn_{0.5}Ga_{0.5}Se_2$ nanocrystalline thin films were thermally evaporated on glass and silicon substrates. The tetragonal chalcopyrite structure with a preferential orientation along the (112) direction was confirmed by X-ray diffraction analysis for CIGS films deposited on glass substrate. The average crystallite size of CIGS absorber layers calculated from XRD data is around 10.3 nm. While, the average grains size obtained from SEM plane-view image is ranged between 115 and 241nm. This suggests that the evaporated CIGS grains contain several individual nanocrystallites. In order to obtain more information on microstructure of the evaporated CIGS layers, the surface of CIGS films deposited on silicon was observed by TEM. From high resolution transmission electronic microscopy image, several atomic plane directions were observed. Additionally, the characteristic interplanar distances of the chalcopyrite phase were extracted from the diffraction rings. Therefore we conclude that from a CIGS nanoparticle, we can obtain nanocrystalline thin films have good structural properties for CIGS solar cells design.

Acknowledgements

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